

The Preparation and Properties of Allyl Pectin

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Allyl ethers of starch (1, 2, 3, 4) and of various other poly-hydroxy compounds (5, 6, 7, 8, 9) have been previously prepared and studied. The properties of these compounds have aroused considerable interest in the paint and varnish industry, with the result that they are now being manufactured on a semi-commercial scale (10, 11). Allyl starch is prepared (1, 3) in the laboratory by the reaction of starch with allyl bromide in the presence of 50 per cent sodium hydroxide solution, with methyl ethyl ketone as solvent. It was anticipated that the substitution of pectin for starch in the above reaction would not result in the etherification of the pectin, since the carboxyl groups in the pectin would be esterified and then saponified, resulting in a continuous conversion of allyl bromide to allyl alcohol. However, it has been possible, with slight alterations in procedure, to produce allyl pectin in moderate yields. The product, isolated from the reaction mixture by steam distillation, is a cream-colored, thick, sticky, pudding-like material, containing a high proportion of moisture, part of which may be separated by freezing. It may be purified by dissolving in ethylene chlorhydrin and reprecipitating in water. Allyl pectin cannot be obtained in the dry condition without alteration. It cannot, like allyl starch, be ground in the frozen state. Its solutions may be dried by azeotropic distillation. For these reasons, chemical analyses were made on the moist material, samples being taken simultaneously for moisture determination by distillation with toluene. The degree of allylation is determined by a Wijs titration, the sample being first dissolved in ethylene chlorhydrin. The allyl content varies from 1.7 to 2.6 groups per galacturonic acid unit, with most values falling between 2.0 and 2.3. Saponification data indicate that a portion of the groups are present as allyl ester (from 13 to 25 per cent of the total allyl content).

Allyl pectin is soluble in most organic solvents, particularly acetone, butanol, and ethylene chlorhydrin. It is insoluble in aliphatic hydrocarbons. Upon standing in air, it gradually becomes darker and more viscous and forms a scum on the surface. Upon heating, it polymerizes and becomes hard.

Experimental

Raw Material: The raw material was an apple pectin containing 8.42 per cent moisture and, on the dry basis, 13.88 per cent ash and 6.88 per cent methoxyl.

Preparation: 300 g. of pectin, 600 ml. of methyl ethyl ketone and 318 ml. of allyl bromide were placed in a 2-liter three-necked flask fitted with a mercury-seal stirrer, a reflux condenser and a dropping funnel. 300 g.

of 50 per cent NaOH solution was added through the funnel in a slow stream to the stirred suspension. The temperature rose to 50°. Vigorous stirring was necessary to prevent lumping. The flask was then heated in a water bath at 80°. After refluxing for five to seven hours, the mixture was cooled, the supernatant liquid was decanted, and the residue washed twice with acetone. The combined decantate and washings were filtered (or centrifuged) and the clear amber solution was steam distilled until the vapor temperature reached 90 to 95°. The residue was cooled and the excess water decanted. The moist allyl pectin was placed in a freezing cabinet until solidly frozen. It was then removed, allowed to thaw at room temperature, and the excess water decanted. Total weight of moist material, 138.4 g.

Purification: The crude moist material was dissolved in the minimum volume of ethylene chlorhydrin. The solution was transferred to a separatory funnel and allowed to stand for several hours. A small amount of insoluble matter rose to the top of the solution. The clear solution was run slowly into 10 volumes of rapidly-stirred water, whereupon the allyl pectin was reprecipitated. The water was decanted and the residue again frozen to reduce the moisture content. The final product weighed 80.9 g. and contained 40.8 per cent moisture. It contained, on the dry basis, 35.2 per cent of allyl group, corresponding to 2.3 groups per galacturonic acid unit.

Preparation of test solution: 75 g. of the above material was dissolved in 150 ml. of n-butanol. In order to insure the elimination of water, the solution was distilled until the vapor temperature reached 115°. The distillation was then continued under vacuum until the viscosity of the residue reached 150 centipoises, as measured by the Gardner bubble viscometer. This solution was dark brown in color, and contained 49.2 per cent solid matter.

Evaluation of films: Test films were prepared from the above solution and evaluated by the methods described by Wrigley, et al. (12). They were cured by heating at 92°, and required 64 hours curing to resist scratching by the fingernail test. These films had a Sward hardness of 40 and an elongation of over 30 per cent. Table 1 shows their resistance to various reagents.

Table 1—Failing Time of Allyl Pectin Films When Subjected to the Action of Various Reagents.

Phenol, 5%	3 minutes
Ammonium hydroxide, 10%	3 minutes
Sodium Hydroxide, 5%	3 minutes
Boiling water	20 minutes
Soapy water, 25° C.	24 hours
Distilled water, 25° C.	>72 hours
Ethyl alcohol, 50%	>72 hours
Acetic acid, 4%	>72 hours
Acetone	>72 hours

The following comparisons of allyl pectin films with those prepared from allyl starch may be made: Allyl pectin requires a much longer curing period than allyl starch. Its films are somewhat below the average of allyl starch films in hardness. They are somewhat above the average in elongation (a test of flexibility). They are less resistant to phenol, ammonium hydroxide, and sodium hydroxide, but more resistant to boiling water, ethyl alcohol, acetic acid and acetone.

Allylation of galacturonic acid: For the purpose of comparison, a sample of crude galacturonic acid was treated as follows: 100 g. of the crude material (85.9 per cent uronic acid) was placed in a one-liter three-necked flask (fitted as before) with 300 ml. of allyl bromide. 100 g. of 50 per cent NaOH was added through the dropping funnel with stirring, and the flask heated on the water bath until the reaction commenced. The bath was removed while the vigorous reaction proceeded, and then replaced. After three hours, the mixture was cooled and transferred to a separatory funnel. The lower (aqueous) layer was drawn off and extracted with ether. The extract was added to the upper layer, and the mixture was steam distilled. The residue was a black, tarry liquid, weighing 14.45 g. and containing 17.30 per cent moisture. It had an allyl content of 48.6 per cent, corresponding to 3.96 allyl groups per molecule of galacturonic acid, of which a little less than one group was present as allyl ester. Films of this material could be hardened somewhat by prolonged heating, but not enough to resist scratching by the fingernail. It was not further investigated.

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Summary

Allyl ethers of pectin were prepared by direct allylation in the presence of a strong solution of sodium hydroxide. The products contained from 1.7 to 2.6 allyl groups per galacturonic acid unit. They could be dissolved in organic solvents, and their solutions could be polymerized by heating, to give hard films.

An allyl ether of galacturonic acid was prepared containing 3.96 allyl groups per molecule.

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